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**(54) Coating apparatus, method of coating glass, compounds and compositions for coating glass and coated glass substrates**

Vorrichtung und Verfahren zum Beschichten von Glas, Verbindungen und Zusammensetzungen zum Beschichten von Glas und beschichtete Glassubstrate

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  - JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 136, no. 6, June 1989, pages 1843-1844, XP000034588 HOCHBERG A K ET AL:

(60) Divisional application:  
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to the chemical nature of the coating.

[0015] From the figure and the specification of this document it is evident that the coating composition is supplied by a central injection passage and is divided into two currents directed upstream and downstream of the nozzle to achieve a relatively thick coating.

5 [0016] EP-A-499 523 discloses a nozzle structure of coating float glass by pyrolysis of a gas mixture. The gas mixture is directed onto the glass surface through a chamber and the excess is removed through chamber. In figures 2 and 3 a second suction line is shown to remove lost gas to avoid contamination of the atmosphere of the float glass chamber.

10 [0017] In US-A-5,122,391 chemical vapor deposition of doped and undoped indium oxide or indium-tin oxide films is disclosed. There is also mentioned to deposit a precoat of  $\text{SiO}_2$ .

[0018] US-A-4,922,853 teaches on line chemical vapor deposition. The metal oxide coatings are prepared by decomposition of a reactant comprising an organo metallic or other metallic compound or mixtures thereof with or without a suitable dopant.

15 [0019] Although each of the apparatuses and processes taught in the above-discussed patents is acceptable for its intended purpose, there are limitations when the apparatuses and processes are used to apply the coating to a moving heated glass substrate, e.g. a glass ribbon supported on a molten metal bath contained in a non-oxidizing atmosphere. It would be advantageous, therefore, to provide apparatuses and processes to deposit the coating on a moving heated substrate as well as the metal containing precursors used in the preparation of the coating.

20 [0020] One of the limitations of the presently available vapor coating system for coating a glass ribbon moving at fast speeds e.g. about 15.24 meters/min. (600 inches/min.) is that the vapor coating mixture does not have sufficient time to deposit a coating of acceptable thickness on the glass ribbon. The article entitled "The LPCVD of Silicon Oxide Films Below 400°C (750°F). From Liquid Sources" by A. K. Hochberg and D. L. O'Meara published in J. Electrochem. Soc. Vol. 136, No. 6, June 1989 copyrighted by The Electrochemical Society, Inc. pps. 1843 and 1844 teaches the use of trimethylphosphite to accelerate coating deposition below 400°C (750°F).

25 [0021] The publication "User's Guide For: Glass Deposition with LTO-410™ Source Material" by Dr. A. Hochberg and Dr. B. Gelernt, copyrighted 1990 by Schumacher of Carlsbad, California, 92009 teaches that the LTO-410 process is not significantly changed with the addition of trimethylphosphite.

[0022] Although the use of accelerants is taught, there are no teachings that such accelerants are beneficial at elevated temperatures e.g. above 400°C (750°F). Therefore it would be advantageous to provide accelerants for coating systems that operate at temperatures above about 536°C (1000°F).

30 [0023] The object of the invention is attained by a transparent substrate having a coating thereon composed of at least two different metal oxides and having greater than 0 and up to 15 atomic percent of an element dispersed therethrough selected from the group consisting of phosphorus, aluminum and boron wherein the mixed metal oxide itself excludes phosphorus, aluminum and boron and the coating has regions of continuously varying ratio of the different metal oxides as the distance from the substrate-coating interface to the opposite surface increases and with the substantial absence of strata of a fixed ratio of the different metal oxides.

35 [0024] The solution includes a method of depositing a vapor-coating composition containing metal precursor compounds onto the surface of a moving substrate by the steps of: directing the vapor coating composition toward a first predetermined position on the surface of the substrate, moving a first portion of the vapor along a first region of the substrate surface in a first direction which is parallel with the direction in which the substrate is moving, and a second portion of the vapor along a second region of the substrate surface in a second direction opposite to the first direction and maintaining the first portion of the coating composition on the first region of the substrate surface for a longer period of time than the second portion of the vapor on the second region of the substrate to coat the substrate, and exhausting the first and second portions of said vapor on each side of said first predetermined position after different periods of contact with the substrate surface, wherein the vapor coating composition contains at least two different metal containing precursors in an oxygen containing carrier gas to provide a coating having a continuously varying chemical composition of metal oxides as the distance from the substrate coating interface to the opposite surface increases.

40 [0025] A further embodiment of the invention relates to a coating apparatus for depositing a vapor coating composition containing metal precursor compounds onto the surface of a moving substrate comprising:

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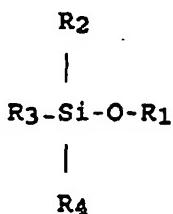
- (i) means for directing a vapor coating composition toward the surface of said substrate,
- (ii) a first exhaust means spaced in a distance "x" from said vapor directing means on one side thereof,
- (iii) a second exhaust means spaced in a distance "y" from said vapor directing means on the other side thereof and in alignment with said vapor directing means and said first exhaust means,
- 55 (iv) a first discharge means on the outboard side of the first exhaust means for directing an inert gas toward the surface of said substrate,
- (v) a second discharge means on the outboard side of the second exhaust means for directing an inert gas toward the surface of said substrate, each of the discharge means providing an inert gas curtain to prevent the coating

vapors from moving from the coating zone between the discharge means into the atmosphere outside of the coating apparatus, and also to prevent the atmosphere from moving into the coating zone.

[0026] The invention relates to a transparent substrate e.g. a glass substrate having a coating thereon composed of mixed metal oxides e.g. silicon oxide and tin oxide. The coating composition has a continuously changing ratio of silicon oxide to tin oxide as the distance from the glass-coating interface increases, e.g. substantially all silicon oxide at the glass coating interface and substantially all tin oxide at the opposite coating surface. Between the glass-coating interface and the opposite coating surface there are minimal, if any, strata of a fixed ratio of silicon oxide to metal oxide and there are dispersed in the coating small amounts of phosphorus, boron, and/or aluminum when compounds containing those elements are used as accelerants to increase the coating deposition rate and control the coating morphology.

[0027] The invention still further relates to a vapor coating composition having a silicon containing precursor having the structural formula

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25 where  $R_1$  is selected from groups that include alkyl and alkenyl.  $R_2$  is the functional group giving the silicon compound the ability to be easily converted to silicon oxide and includes hydrogen, halogen, alkenyl and halogenated alkyl radicals.  $R_3$  is a bridging group to provide for multiple silicon atom compounds and includes -S- and

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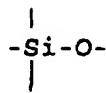
-N-

35

groups.  $R_4$  completes the bonding of the foundation silicon atom.

[0028] Also, the invention relates to a coating composition having mixed metal containing precursors e.g. tin and silicon containing presursors. The silicon metal precursor may include

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containing compounds described above and an accelerant capable of enhancing the reaction rate of the coating compounds. The accelerants include Lewis acids and Lewis bases.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Figure 1 illustrates a coated substrate incorporating features of the invention and obtained using the apparatuses, processes, and coating materials of the invention.

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[0030] Figure 2 is an elevation view of a coating system having two coating stations, one of which includes a coating apparatus having multiple coating zones incorporating features of the invention.

[0031] Figure 3 is a view similar to that of Figure 2 of a coating apparatus having one coating zone incorporating features of the invention.

[0032] Figure 4 is a graph showing a gradient coating and an extended and improved gradient coating deposited in accordance with the teachings of the invention.

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[0033] Figure 5 is a graph showing the effect of coating apparatus height from the surface of a glass substrate and carrier flow on the ratio of tin oxide to silicon oxide in the coating deposited on the glass substrate in accordance with the teachings of the invention.

[0034] Figure 6 is a graph showing the effect on film thickness using the accelerants of the instant invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0035] Referring to Figure 1, there is shown a coated article 10 incorporating features of the invention that can be made using the apparatuses, processes, and coating materials, of the invention. In general, the article 10 includes a substrate 12, e.g. but not limiting to the invention, plastic and/or clear or colored glass, having a coating 14 that exhibits minimum reflected color by having a continually varying refractive index, and preferably has an emissivity lower than the uncoated substrate. In the following discussion the substrate is a glass substrate. The coating 14, in general, is composed of a mixture of silicon oxide and a metal oxide, such as tin oxide. As with Zaromb, discussed above, the coating 14 has a continuously changing composition as the distance from the glass-coating interface 16 increases.

5 Generally, near the glass-coating interface 16, the coating is predominantly silicon oxide, while at the opposite surface 18 of the coating 14 e.g. the coating surface farthest from the glass-coating interface 16, the composition of the coating is predominantly tin oxide. The predominantly tin oxide region may continue as predominantly tin oxide for a thickness required by the use of the article. For example when an article having a high emissivity is desired e.g. close to the emissivity of the glass substrate, the predominantly tin oxide region is thin; when an article having a low emissivity is desired, the predominantly tin oxide region is thicker. The tin oxide region may be doped with fluorine or antimony as taught in U S -A- 3,677,814 to further reduce emissivity. Between the glass-coating interface 16 and opposite surface 18, the coating 14 is composed of continuously varying amounts of silicon oxide and tin oxide as the distance from the glass-coating interface 16 increases. In other words, as the distance from the glass-coating interface 16 increases, each succeeding region of the continuously varying composition in the coating 14 contains a tin oxide to silicon oxide 10 weight percent ratio different than the preceding region and although not limiting to the invention, usually that ratio tends to increase as the distance from glass-coating interface 16 increases. The opposite surface 18 is predominantly tin oxide, i.e., the weight percent of silicon oxide in the outermost region approaches zero, and the weight percent of tin oxide approaches 100.

15 [0036] Although the coating 14 was discussed using a coating of tin oxide and silicon oxide, the invention is not limited thereto and as will be appreciated from the discussion below any two or more different metal oxides may be used in the practice of the invention.

20 [0037] The coated article 10 of Figure 1 was produced using coating system 19 shown in Figure 2. A discussion of coating apparatus 20 in Figure 3 will now be presented for a better appreciation of the features of the coating system 25 shown in Figure 2. The apparatus 20 of Figure 3 may be used to deposit a non-homogeneous coating of the type 30 discussed above on the glass substrate 12. In Figure 3 as in Figure 2, the substrate 12 is a glass ribbon 22 or pieces cut therefrom.

35 [0038] With reference to Figure 3, coating apparatus 20 is supported in any convenient manner above and spaced from the glass ribbon 22 supported on a pool or bath 24 of molten metal contained in a chamber having a non-oxidizing atmosphere, not shown, e.g. of the type of chamber taught in U S -A-4,853,257. As viewed in Figure 3, the glass ribbon 22 moves from left to right beneath the coating apparatus 20 e.g. through a coating position. As will be appreciated the invention is not limited to the chamber, not shown, containing the pool of molten metal, nor to a non-oxidizing atmosphere and any chamber design having any type of atmosphere as well as other processes for moving a heated substrate past a coating apparatus embodying features of the invention may be used in the practice of the invention.

40 [0039] In general and not limiting to the invention, the ribbon 22 has a thickness range from about 0.08 inch to about 0.50 inch (about 2 to about 13 millimeters) and moves at speeds of about 700 to about 100 inches (about 17.80 meters to about 2.54 meters) per minute, respectively. The molten tin bath 24 has a temperature in the range of about 1000°F (538°C) to about 1094°C (2000°F).

45 [0040] The apparatus 20 includes an elongated coating unit 25, two elongated exhausts 28 and 26, one on each side of the coating unit 25, and two elongated discharge units 31 and 32, one on each outboard side of an exhaust as shown in Figure 3. The term "elongated" as used herein means that the coating unit, exhausts and discharge units extend across the width of the ribbon i.e. transverse to the movement of the ribbon 22. The discharge units 31 and 32 provide an inert gas curtain to prevent the coating vapors from the coating zone, i.e. the zone between the discharge units 31 and 32, from moving into the chamber atmosphere and also to prevent the chamber atmosphere from moving into the coating zone. As can be appreciated the separation between the coating zone and chamber atmosphere is 50 required because the atmosphere in the coating zone as will be discussed is an oxidizing atmosphere, and the chamber atmosphere as discussed above is a non-oxidizing atmosphere. In the practice of the invention, the inert gas was nitrogen.

55 [0041] The exhausts 26 and 28 in accordance with the teachings of the invention are not equally spaced from the coating unit 25. More particularly, with the glass ribbon moving from left to right as shown in Figure 3, the exhaust 28 is closer to the coating unit 25 than the exhaust 26. By positioning the exhausts at different distances from the coating unit the coating vapors are in contact with the ribbon surface for different periods of time. Therefore, all other parameters being equal, e.g., glass temperature, spacing between the coating unit and glass ribbon surface and exhaust pressures, a thicker coating will be deposited on the ribbon as it passes between the exhaust 26 and the coating unit 25, than

between the coating unit 25 and the exhaust 28. This feature of the invention will be more fully appreciated in the discussion of the coating system 19 shown in Figure 2.

[0042] As can now be appreciated, the design of the discharge units 31 and 32, the exhausts 26 and 28 and coating unit 25 are not limiting to the invention. The invention has been practiced using the exhausts 26 and 28 with an elongated opening 36 connected to a collection chamber 38 and using the discharge units 31 and 32 with an elongated opening 50 connected to a discharge chamber 46. The inert gas has uniform pressure and constant velocity along the length of the opening 50 to provide a curtain of inert gas, a portion of which flows into the chamber (not shown) atmosphere and a portion toward the adjacent exhaust 26 or 28 as shown in Figure 3.

[0043] The coating unit 25 includes a discharge chamber 56. The coating vapor exits the chamber 56 by way of elongated opening 58 and is directed toward the surface of the glass ribbon 22 passing beneath the opening 58. The coating vapor has a uniform pressure and constant velocity along the length of the opening 58 and has sufficient pressure to allow a portion of the coating vapor to flow upstream and a portion to flow downstream as viewed in Figure 3.

[0044] The amount of nitrogen typically introduced by each discharge unit 31 and 32 ranges from 20 to 300 standard cubic feet per minute for a ribbon having a width of about 4.06 meters (160 inches). As can be appreciated the flow rate of the nitrogen is not limiting to the invention; however, it should be sufficient to provide an inert curtain separating the coating zone and the chamber atmosphere.

[0045] The openings 36 of the exhausts 26 and 28 and the exhaust pressure is adjusted to exhaust a portion of the inert gas from the adjacent discharge unit 31 and 32, respectively, and a portion of the coating vapor from the coating unit 25. As seen in Figure 3 and as discussed above, the exhaust 26 is spaced further from the coating unit 25 than the exhaust 28. With this arrangement and maintaining the exhaust pressure the same for each exhaust unit, the coating vapor residence time is greater for the glass ribbon 22 as it moves from the exhaust 26 toward the coater unit 25 than for the glass ribbon as it moves from the coater unit 25 toward the exhaust 28.

[0046] Although the above asymmetric arrangement is preferred, because of the simplicity thereof, the invention is not intended to be so bound, since the discovery herein resides in the fact that having different coating vapor residence times on different sides of a coater unit alters the final composition of the coating. Therefore, other apparatuses or processes suitable for obtaining such an effect can be used. It has been determined that the same effect achieved with asymmetrically arranged exhausts, as discussed above, can also be achieved, even with symmetric spacing of the coating unit 25 and the exhausts by, for example, adjustment of the height or level of the openings 36 of the exhausts 26 and 28 relative to one another and to the glass ribbon. Another method to vary the coating vapor residence time is to vary the ratio of the flow of the exhaust 26 to the exhaust 28.

[0047] By way of illustration only, in the instance when the spacing between the coating unit 25 and exhausts 26 and 28 is symmetrical, reducing the pressure of the exhaust 26 below the pressure of the exhaust 28, results in the coating vapor residence time between the coating unit 25 and exhaust 26 being greater than the coating vapor residence time between the coating unit 25 and the exhaust 28.

[0048] Referring now to Figure 2, the coating system 19 was used to apply the coating 14 of the coated article 10 shown in Figure 1. The coating system 19 includes a coating station 59 for applying a compositionally graded coating and coating station 60 for extending the thickness of the predominantly tin oxide region at the surface 18 of the coating 14 (see Figure 1). The coating station 59 includes coating units 61, 62 and 64, exhausts 66, 68, 70 and 72 and discharge units 31 and 32. The coating station 60 is not limiting to the invention; however the coating station used in the practice of the invention was the type of coating apparatus disclosed in U.S. -A- 4,853,257 which teachings are hereby incorporated by reference. Opening 50 of the discharge unit 31 is spaced about 63.5 cm (25 inches) from opening 50 of the discharge unit 32; opening 74 of the exhaust 66 is spaced about 57 cm (22-1/2 inches) from the opening 50 of the discharge unit 32; opening 76 of the coating unit 61 is spaced about 51 centimeters (20 inches) from the opening 50 of the discharge unit 32; opening 78 of the exhaust 68 is spaced 44.5 cm (17-1/2 inches) from the opening 50 of the discharge unit 32; opening 80 of the coating unit 62 is spaced about (12-1/2 inches) 32 centimeters from the opening 50 of the discharge unit 32; opening 82 of the exhaust 70 is spaced about (10 inches) 25.4 centimeters from the opening 50 of the discharge unit 32; opening 84 of the coating unit 64 is spaced about (5 inches) 12.7 centimeters from the opening 50 of the discharge unit 32, and opening 86 of the exhaust 72 is spaced about 6 centimeters (2-1/2 inches) from the opening 50 of the discharge unit 32. The coating station 60 was spaced about (6 feet) 1.8 meters from the discharge unit 32.

[0049] The openings 50, 74, 76, 78, 80, 82, 84, and 86 were spaced, in a convenient manner, about 0.51 cm (0.2 inches) above the upper surface of the glass ribbon 22 as viewed in Figure 2. The length of the openings 50 was about 64 centimeters (25 inches); the length of the openings 74, 78, 82 and 86 was about 64 centimeters (25 inches) and the length of the openings 76, 80 and 84 was about 53.34 cm (21 inches). The width of the openings 50 was about (0.125 inch) 0.32 centimeter; the width of the openings 74, 78, 82 and 86 was about 0.64 centimeter (0.250 inch) and the width of the openings 76, 80 and 84 was about 0.15 cm (0.06 inch). The flows of nitrogen and coating vapor were about 350 to about 700 SLPM (standard liters per minute). The exhaust flow was about 375 to about 770 SLPM. The glass ribbon speeds were between about 5.08-17.78 m (200-700 inches) per minute, the temperature of the glass

ribbon moving into, through and out of the coating stations 59 and 60 was between about 635-675°C (1170-1250°F). [0050] The coating system 19 and in particular the coating station 59 and the method associated therewith are especially effective for the chemical vapor deposition (CVD) of coatings from mixtures of silicon and metal containing precursors to provide the article 19 shown in Figure 1.

5 [0051] In the following discussion, the coating 14 is made from a mixture of tin containing precursors and silicon containing precursors capable of being volatilized and converted to their corresponding oxides in the presence of oxygen at temperatures in the range of (750° to 1500°F) 400°C to 815°C. As will be appreciated the invention is not limited thereto and other metal containing precursors may be used with the coating apparatus and in the coating processes discussed above.

10 [0052] Examples of silicon compounds that may be used in the practice of the invention include, but are not limited to, tetraethoxysilane, silane, diethylsilane, di-t-butoxydiacetoxysilane and the silicon compounds disclosed in U.S. -A (S)- 3,378,396 to Zaromb and U.S. -A(S)- 4,187,336, 4,308,316, 4,377,613, 4,419,386, 4,206,252, 4,440,822, and 4,386,117.

15 [0053] Compounds that have been used in the practice of the invention include diethylsilane, tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, diethyldichlorosilane, tetramethylcyclotetrasiloxane and triethoxysilane.

[0054] In addition to the silicon containing precursors discussed above, the invention contemplates silicon containing precursors that can be converted to their corresponding silicon oxides and can be used in admixture with the metal containing precursors to form the desired coating on a substrate e.g. a glass substrate having a coating with the desired mixed oxide gradient.

20 [0055] When looking for a silicon containing precursor to form a silicon oxide coating, one skilled in the art would not normally choose a precursor having an Si-O bond because it is one of the strongest bonds in nature to break, as is evidenced by the stability of the mineral quartz (SiO<sub>2</sub>). Therefore breaking the Si-O bond in the precursor and rearranging it into a network lattice containing the silicon oxide bonds desired for a coating is difficult e.g. the siloxane bond requires high temperature and/or long periods of time to form a corresponding silicon oxide coating. For this reason silicon containing precursors having the siloxane structure would not be expected by one skilled in the art to be useful in the formation of a silicon oxide coating on a moving substrate.

25 [0056] It has been determined, however, that if a compound carrying an Si-O bond also carries at least one specific functional group, the reactivity of the silicon containing precursor having the Si-O bond, and therefore its coating formation rate, will be increased, even though the bond strengths would not seem to indicate any appreciable change in its coating formation behavior. The functional groups that are capable of giving the silicon containing precursor containing an Si-O bond the ability to be easily converted to a silicon oxide coating include hydrogen, halogens, vinyls and α-chlorinated alkyls. The reactivity of the silicon containing precursor can then be tailored by the appropriate choice of functional groups. The silicon containing precursor of the instant invention is not limited to having only the above-defined substituents thereon. As long as one or more of the above-defined functional groups is present on the silicon containing precursor carrying the Si-O bond, other groups, such as alkyls and other substituents more fully defined below, can also be present without a significant deleterious effect on the overall reactivity of the silicon containing precursor.

30 [0057] Compounds bearing the Si-O bond can be exemplified by reference to the following structural formula I:

40

I

R<sub>2</sub>

|

R<sub>3</sub>-Si-O-R<sub>1</sub>

|

R<sub>4</sub>

45

wherein R<sub>1</sub> is selected from the following Group A which consists of compounds that do not have an oxygen available to form the peroxide bond:

50 alkyl, or substituted alkyl, radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>2</sub>OH;  
 55 halogenated or perhalogenated alkyl radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as -CCl<sub>3</sub>, -CH<sub>2</sub>CHClCH<sub>3</sub> and -CH<sub>2</sub>CCl<sub>2</sub>CCl<sub>3</sub>;  
 alkenyl or substituted alkenyl radicals having from 2 to 10, preferably 2 to 4, carbon atoms, such as -CH=CHCH<sub>3</sub>

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and -CH=CH<sub>2</sub>;  
alkynyl or substituted alkynyl radicals having from 2 to 10, preferably 2 to 4, carbon atoms, such as -C≡C-CH<sub>3</sub> and -C≡CH; and  
5 aryl or aralkyl or substituted aryl or aralkyl radicals having from 6 to 11, preferably 6 to 9, carbon atoms, such as -C<sub>6</sub>H<sub>5</sub> and -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>;

wherein R<sub>2</sub> are functional groups that form a bond with the Si atom which is easily thermally broken e.g. at temperatures between 93.5°C-445°C (200°F-800°F) and preferably between 205°C-370°C (400°F-700°F). The functional group (R<sub>2</sub>) capable of giving the silicon containing precursor the ability to be easily converted to a silicon oxide coating is  
10 selected from Group B consisting of:

hydrogen;  
halogen, preferably Cl;  
15 alkenyl or substituted alkenyl radicals as defined in Group A for R<sub>1</sub>;  
α-halogenated alkyl or perhalogenated alkyl, and  
alkynyl or substituted alkynyl radicals as defined in Group A for R<sub>1</sub>;

wherein R<sub>3</sub> is a bridging group to provide for multiple silicon atom compounds. R<sub>3</sub> is selected from Group C consisting  
of:  
20 -S-;

-N-R<sub>5</sub>

25 wherein R<sub>5</sub> is an alkyl or substituted alkyl radical  
having from 1 to 10, preferably 1 to 4, carbon atoms, such as -CH<sub>2</sub>CH<sub>3</sub> or -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>;

30 -N-;

35 -P-H;

40 -P-R<sub>5</sub>

45 wherein R<sub>5</sub> is as defined above.

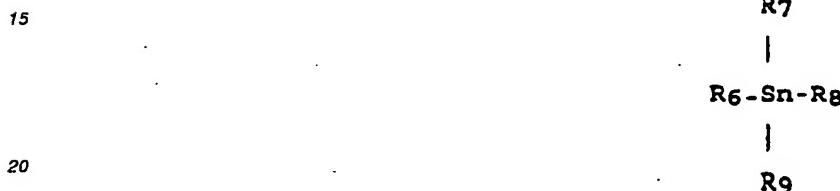
50 -P-



loxane, triethoxysilane, chlorotriethoxysilane, pentachloroethyltriethoxysilane and vinyltriethoxysilane.

[0063] Metal containing precursors that can be used in admixture with the silicon containing precursors defined above in the chemical vapor deposition of mixed oxides on a glass substrate include metal containing precursors that are vaporizable at or below about 260°C (500°F) and that will react with an oxygen-containing gas to form the corresponding metal oxides. Preferably, but not limiting to the invention, compounds that may be used include organometallic compounds containing metals including but not limited to titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, arsenic, selenium, yttrium, zirconium, niobium, molybdenum, cadmium, rhodium, ruthenium, palladium, indium, antimony, tellurium, tantalum, tungsten, platinum, lead, bismuth, aluminum, and tin. Of these metal compounds, tin compounds are most preferred. Examples of tin compounds useable herein include those defined by the following structural formula II:

## II



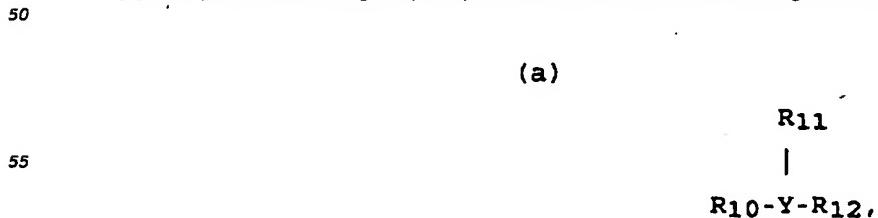
wherein R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> are the same or different and include but are not limited to halogens preferably Cl or F, an alkyl radical having from 1 to 10, preferably 1 to 4, carbon preferably 6 to 9, carbon atoms, such as -C<sub>6</sub>H<sub>5</sub>. In the practice of the invention any other organic or inorganic functional group can be used provided the vapor pressure of the resultant compound is at least 0.01 pounds per square inch absolute, below about 260°C (500°F).

[0064] The silicon containing precursors defined above, including those bearing the Si-O bond, can be used alone, or they can be used in admixture with the organometallic compounds discussed above in the chemical vapor deposition of the corresponding single or mixed oxides on a glass substrate. However, when the silicon containing precursor is used alone, or in admixture with other metal containing precursors, in the chemical vapor deposition of single or mixed oxides onto a moving substrate e.g. coating a ribbon of glass advancing along a molten metal bath or on a conveyor, it is desirable to have a rate of silicon oxide deposition sufficient to coat the moving glass substrate. For example, when coating an advancing glass ribbon and the deposition rate of silicon oxide is relatively low, the glass ribbon speed has to be reduced. More particularly, to deposit about a 1200 Å thick coating on a glass ribbon moving at a line speed of greater than about 7.62 meters (300 inches) per minute, the rate of deposition of all classes of silicon containing precursors used in the chemical vapor deposition processes has to be increased to attain a uniform coating.

[0065] A number of materials have been identified that can be used to accelerate the deposition rate of silicon oxides from their precursors. The type and functionality of each accelerant depends to some extent on the silicon containing precursors with which it will be used. Combinations have been determined for a specific coated article and for the process used to deposit the desired coating, in particular, the mixed oxide of the invention. It has further been determined that a synergistic effect occurs between certain combinations of precursors and accelerants that result in a beneficial altering and control of the morphology of the coating.

[0066] Accelerants that can be used in the practice of the invention to increase the deposition rate of silicon oxide alone or in combination with another oxide, for example, tin oxide, can be defined as follows:

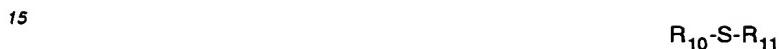
- 45  
(1) Lewis Acids, such as trifluoroacetic acid and hydrochloric acid.  
(2) Lewis Bases, such as NaOH, NaF, CH<sub>3</sub>OH, CH<sub>3</sub>OCH<sub>3</sub> and S(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>.  
(3) Water.  
(4) Compounds of nitrogen, phosphorus, boron, and sulfur having the following structural formulae:



(b)



(c)



(d)



30 and

(e)



45 wherein Y is selected from the group consisting of nitrogen, boron and phosphorus and  $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{12}$ ,  $\text{R}_{13}$  and  $\text{R}_{14}$  are selected from the following list of functional groups, hereinafter referred to as Group F:

hydrogen;  
 halogens, preferably Cl;  
 50 alkanyl or substituted alkanyl radicals having from 2 to 10, preferably 2 to 4, carbon atoms, such as  $-\text{CH}=\text{CH}_2$ ; perhalogenated alkyl or substituted alkyl radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as  $-\text{CCl}_2\text{H}_2$  or halogenated alkyl or substituted alkyl radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as  $-\text{CCl}_2\text{CH}_2\text{CH}_3$ ;  
 acyloxy radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as  $-\text{OCOCH}_3$ ;  
 alkynyl or substituted alkynyl radicals having from 2 to 10, preferably 2 to 4, carbon atoms, such as  $-\text{C}\equiv\text{CH}$ ;  
 55 alkyl or substituted alkyl radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ;  
 aryl or substituted aryl radicals having from 6 to 10, preferably 6 to 9, carbon atoms, such as  $-\text{C}_6\text{H}_4\text{CH}_3$ ;  
 alkoxide or substituted alkoxide radicals having from 1 to 10, preferably 1 to 4, carbon atoms, such as

-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>;

wherein said substituents are from Group E discussed above,  
examples of which compounds include but are not limited to triethylphosphite, trimethylphosphite, trimethylborate,  
5 PF<sub>5</sub>, PCl<sub>3</sub>, PBr<sub>3</sub>, PCl<sub>5</sub>, BCl<sub>3</sub>, BF<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>BBR, SF<sub>4</sub> and HO<sub>3</sub>SF. In the practice of the invention triethylphosphite  
was used.

(5) Compounds of aluminum having the following structural formula III may be used to accelerate the deposition  
rate of silicon containing precursors alone or in combination with other metal containing precursors (the "other  
metal containing precursors", as can be appreciated, do not include aluminum containing precursors):

10

## III

R<sub>15</sub>

15

R<sub>17</sub>-Al-R<sub>16</sub>

wherein R<sub>15</sub>, R<sub>16</sub>, and R<sub>17</sub> are the same or different and are selected from the following Group G:

20

hydrogen;  
halogens, preferably Cl;  
-O-R<sub>17</sub>, wherein R<sub>17</sub> is a linear, branched or substituted alkyl radical having from 1 to 10 carbon atoms, preferably 1 to 4, with substituents selected from Group E discussed above;  
25 -S-R<sub>18</sub>, where R<sub>18</sub> is equivalent to R<sub>17</sub> defined above;  
-NH<sub>2</sub>;  
R<sub>19</sub>-N-R<sub>20</sub>, wherein R<sub>19</sub> and R<sub>20</sub> are linear or branched alkyl groups, or substituted alkyl groups having from 1 to 10, preferably 1 to 4, carbon atoms, with substituents selected from Group E discussed above; (less the phosphine groups, such as -PH<sub>2</sub>); and  
30 N R<sub>21</sub>, wherein R<sub>21</sub> forms cyclic group having from 2 to 10 preferably 2 to 6 carbon atoms, with substituents selected from Group E discussed above (less the phosphine groups).

(6) Ozone.

35 [0067] The mechanism that causes the accelerants of the invention to increase the rate of deposition is not completely understood. Even though the mechanism is not completely understood the results, discussed below, clearly demonstrate that the mixed oxide coating deposition rate was increased. With reference to Table 2 in Example I below, Run Nos. 11 and 12 contain the accelerant triethylphosphite. The growth rate of the silicon oxide coating was at least twice the rate of the silicon oxide coating of Run No. 2 that did not have an accelerant.

40 [0068] A moving glass substrate was coated using the same precursor chemistry as used in Run Nos. 11 and 12 of Table 2 and similar deposition rates resulted. The precursors were vaporized at a temperature of (150°F) 65°C to 260°C (500°F), and the gaseous mixture of the precursors, oxygen containing gases, and carrier gas and accelerant, were brought into contact with a glass ribbon supported on a molten metal bath and heated to a temperature of about 510°C (950°F) to about 730°C (1350°F). The glass ribbon advanced at a speed of 4.25 to 18.00 meters (170 to 730 inches) per minute.

45 [0069] The amounts of the components that may be used in the practice of the invention are defined below in Table 1.

Table 1

	<u>Compound</u>	<u>Mole Percent</u>	
		Broad Range	Preferred Range
	Metal Containing Precursor	0.005 to 5.0	0.1 to 2.0
	Silicon Containing Precursor	0.0001 to 5.0	0.05 to 2.0
	Oxygen-Containing Gas	1.0 to 99.0	5.0 to 50.0
50	Accelerant	0.0001 to 10.00	0.01 to 2.0
55			

[0070] When the substrate 12 (see Figure 1) e.g. glass substrate is subjected to chemical vapor deposition of mixed

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oxides, for example, a mixture of silicon oxide and tin oxide, to obtain the coating 14 thereon in accordance with the process of the invention, the coating 14, as discussed above, is characterized by having a continuously varying composition as the distance from the glass-coating interface 16 increases, resulting in a substantial reduction of iridescence in the coated product. Assuming a coating composed of substantially silicon oxide and tin oxide, that portion of the 5 coating adjacent to the glass-coating interface 16 is composed largely of silicon oxide and as the distance from the glass-coating composition increases, each succeeding region of the continuously varying composition contains a silicon oxide to tin oxide ratio that varies as the distance from the glass-coating interface increases. More particularly, the percent of silicon oxide decreases as the percent of tin oxide increases, so that as the opposite surface 18 is reached, the region is composed predominantly of tin oxide. Thereafter the thickness of the region of predominantly tin oxide 10 may be increased to reduce the emissivity of the coated article.

[0071] It has been determined that when chemical vapor deposition of mixed oxides on a glass substrate is carried out with the addition of one or more of the accelerants of the instant invention e.g. compounds of phosphorus, aluminum, or boron, a small amount of the foundation atom e.g. phosphorus, aluminum or boron is found dispersed in the coating 14. The presence of phosphorus, aluminum and/or boron in the coating affects the morphology of the resultant coating 15 so that the aforementioned continuously changing components have a decreased probability of forming strata with discrete composition e.g. layers that have a fixed ratio of silicon oxide to tin oxide for thicknesses greater than about 70 Å. Additionally, the presence of phosphorus, aluminum and/or boron affects the morphology of the resultant coating by decreasing the percent crystallinity (approaching 0% crystallinity) and thereby reduces the light scattering properties which can be observed as haze. The amount of the phosphorus, aluminum or boron compound incorporated in the 20 layer is a function of process variables. In the practice of the invention a glass ribbon moving at speeds between 425 to 1800 centimeters (175 to 730 inches) per minute, and having a temperature in the range of 637°C (1180°F) to 660°C (1220°F) was coated with a gaseous mixture having a phosphorus compound as an accelerant; the mole fraction of the accelerant was 0.01 to 0.5. One to 12 atomic percent of phosphorus was found dispersed in the coating. The 25 invention encompasses using an amount of accelerant greater than 0 and up to 15 atomic percent with a preferred range of 1 to 5 atomic percent.

[0072] The present invention will be further appreciated and understood from the description of specific examples which follow:

EXAMPLE I

[0073] A number of compositions were prepared from silicon containing precursors and monobutyltinchloride to illustrate the increased growth rate of mixed oxide films on a glass substrate in accordance with the teachings of the invention. In each composition, monobutyltinchloride was used with different silicon containing precursors. The 30 precursors were vaporized, when necessary, and the resulting gaseous mixture of precursors, oxygen and nitrogen, were introduced into a quartz tube that was electrically heated and controlled to maintain a temperature of 150°C (300°F). The concentration of the silicon containing precursors was in all instances 0.30 mole percent, the monobutyltinchloride 0.50 mole percent, oxygen 21 mole percent, with the remainder nitrogen. The velocity of the precursors and carrier 35 gas was maintained at a rate of 30 centimeters per second in the quartz tube. This gas mixture was passed over a glass substrate heated to about 650°C (1200°F), for 3 to 30 seconds after which the spent gas mixture was vented into a chemical hood. The film thickness for all the runs except Run No. 8 discussed below was measured using a Tencor P1 profilometer. The film growth rate was calculated by dividing film thickness by the coating time. The data 40 obtained are set forth below in Table 2.

Table 2

Run No.	Silicon Containing Precursors	Growth Rate, Å/Second
1	diethysilane	129
2	tetraethoxysilane	43
3	di-t-butoxydiacetosilane	64
4	tetramethylcyclotetrasiloxane	181
5	tetramethylcyclotetrasiloxane	205
6	tetramethylcyclotetrasiloxane	177
7	tetramethyldisiloxane	164
8	ethyltriacetoxy silane	110*
9	triethoxysilane	139

\*estimated

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Table 2 (continued)

Run No.	Silicon Containing Precursors	Growth Rate, Å/Second
10	methyldiacetoxysilane	32
11	tetraethoxysilane + 0.31 mole percent triethylphosphite	136
12	tetraethoxysilane + 0.09 mole percent triethylphosphite	87

[0074] Run No. 1 was used as the control because the diethylsilane is generally accepted as having an acceptable rate of deposition.

[0075] The tetramethylcyclotetrasiloxane precursors used in Run Nos. 4, 5 and 6 were obtained from different suppliers. Run Nos. 2, 3 and 10 using silicon containing precursors having an Si-O bond without the accelerants or the functional groups of the instant invention had an expected low growth rate. Run Nos. 4, 5, 6, 7 and 9 which had a Si-O bond with the functional group of the instant invention had a deposition rate equal to or better than the control Run No. 1. Additionally Run No. 2 when augmented with an accelerator as taught in the instant invention (see Run Nos. 11 and 12) exhibited a deposition rate greater than Run No. 2 and approaching (Run No. 12) or exceeding (Run No. 11) the deposition rate of control Run No. 1.

[0076] Run No. 8 is a compound having the Si-O bond that does not contain a functional group or accelerant of the instant invention; however, it showed a deposition rate equal to the control Run No. 1. The film quality of Run No. 8 was extremely poor and the film thickness had to be estimated using interference colors which was different from the measuring technique used for Run Nos. 1-7 and 9-12.

EXAMPLE II

[0077] Two runs were carried out showing the advantages obtained using an asymmetric coater configuration of the instant invention in place of a symmetric coater configuration. Referring to Figure 3, in one run the exhausts 26 and 28 were positioned relative to the coating unit 25 such that  $x/y=2$  where "x" is the distance between the exhaust 28 and the coating unit 25 and "y" is the distance between the coating unit 25 and the exhaust 26, while in the other embodiment, the exhausts 26 and 28 were positioned relative to the coating unit 25 such that  $x/y=1$ . The coating composition vapor was maintained at 166°C (337°F) and contained 1.2 mole percent monobutyltinchloride, 0.3 mole percent tetraethoxysilane, 0.5 mole percent triethylphosphite, 1.0 mole percent water, 20 mole percent oxygen, and the balance nitrogen. The soda-lime-silica float glass ribbon supported by and moving along a molten metal bath had a thickness of about 0.300 centimeter (0.118 inch), a temperature of about 650°C (1200°F), and a line speed of (510 inches) 13 meters per minute. The surface of the openings of the nitrogen curtain provided by the discharge units 31 and 32 and the exhausts 26 and 28 were maintained at a height of about 0.55 cm (0.22 inch) above the surface to be coated of the glass ribbon-2.

[0078] The tin depth profile of a film produced on the glass ribbon using both the asymmetric and symmetric coater configurations is shown in the graph in Figure 4. The film analysis was accomplished using the Rutherford Backscattering Spectrometry (RBS) technique for purposes of comparing the gradient film produced by the two coater configurations. The RBS spectra in Figure 4 were taken at a special angle in order to obtain optimum depth resolution of the tin atom distribution through the film.

[0079] A comparison of the asymmetric coater configuration (shown by solid line 210) with that of the symmetric coater configuration (shown by dotted line 212) is shown in the RBS spectra in Figure 4. Of significance between the two tin depth profiles 210 and 212 is the extended region of the tin signal from 2025 keV at 3.7 relative counts down to 1890 keV at 1.4 relative counts as compared to the symmetric coater which has its tin signal varying from 2025 KeV at 3.6 relative counts down to 1940 keV at 1.4 relative counts. This difference shows an increase in film thickness for an asymmetric coater configuration. As can be seen from Figure 4 the asymmetric coater configuration provides the gradiant coating with an extended range of varying composition.

EXAMPLE III

[0080] A series of runs was carried out using the coating apparatus 20 of Figure 3 where the exhausts 26 and 28 were positioned relative to the coating apparatus 20 such that  $x/y=1$ . The coating composition vapor was maintained at 165°C (320°F) and contained 0.8 mole percent monobutyltinchloride, 0.3 mole percent tetraethoxysilane, 0.1 mole percent triethylphosphite, 0.54 mole percent water, with the balance air. The total gas flow and coater height were varied while the concentrations were held constant. The results obtained are set forth in the process contour chart in Figure 5. By altering coater height in inches and carrier flow in standard liters per minute, the boundary layer conditions are altered in the coating zone thereby altering the relative ratio of tin oxide and silicon oxide deposited. The process

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contour chart shows how these two other techniques i.e. coater height and volumetric feed, alter the coating composition on the glass substrate.

[0081] As shown in Figure 5 increasing the carrier flow for a given coating unit height, increases the ratio of tin oxide to silicon oxide. In other words, the weight percent of tin oxide increases as the weight percent of silicon oxide decreases. Raising the coating unit height for a given carrier flow decreases the ratio of tin oxide to silicon oxide i.e. the weight percent of tin oxide decreases as the weight percent of silicon oxide increases.

### EXAMPLE IV

[0082] A number of runs were carried out to show the effects of water and triethylphosphite on the thickness of a mixed oxide film at a constant vapor residence time. The process chart, Figure 6, was developed using experimental design data. The coating unit 25 shown in Figure 3 was used with the exhausts 26 and 28 positioned relative to the coating unit 25 such that  $x/y=1$ . The precursor vapor was maintained at  $165^{\circ}\text{C}$  ( $320^{\circ}\text{F}$ ) and contained 0.8 mole percent monobutyltinchloride, 0.3 mole percent tetraethoxysilane. Triethylphosphite (TEP) and water were varied and sufficient air was added to obtain a volumetric feed rate of 500 standard liters per minute. The glass ribbon 22 had a thickness of 0.300 centimeter (0.118 inch), a temperature of  $650^{\circ}\text{C}$  ( $1200^{\circ}\text{F}$ ) and a line speed of 13 meters (510 inches) per minute. The coating unit 25 was maintained at a height of 0.56 cm (0.22 inch) above the surface of the glass ribbon. Note the substantial effect exhibited by the presence of triethylphosphite on the coating thickness. As the mole percent of triethylphosphite was increased the coating thickness increased. Increasing the mole percent of the water also increased the coating thickness.

### EXAMPLE V

[0083] The article 12 of Figure 1 was produced using the coating station 59 shown in Figure 2, in conjunction with the coating station 60 described in the teachings of Henery. Coated articles were produced at three glass thicknesses i.e. at three different glass ribbon speeds to demonstrate the flexibility of the process. The coating station 59 was used to produce a coating that varied in composition from predominantly silicon oxide at the glass-coating interface 16 to predominantly pure tin oxide and the coating station 60 produced an extended thickness of predominantly tin oxide.

[0084] The coating station 59 had three coating units 61, 62 and 64 with openings 76, 80 and 84 respectively, and four exhausts 66, 68, 70 and 72. The exhausts 66 and 68 were positioned relative to the coating unit 61 in a symmetric configuration while the exhausts 68 and 70 and the exhausts 70 and 72 were arranged in an asymmetric configuration about their respective coater units 62 and 64. In addition the coating station 59 had two discharge units 31 and 32 each with opening 50. The distance between the openings 74 and 76, 76 and 78, 80 and 82, 84 and 86 was about 7.08 cm (2-3/4 inches).

[0085] The distance between the openings 80 and 78, and between 84 and 82 was about 14.0 cm (5-1/2 inches).

[0086] To effect the desired change in composition of the coating, different chemical feed rate ranges are required in each of the coating units 61, 62 and 64. The chemical concentrations required to produce the desired compositional change are also a function of the speed of the glass ribbon. Examples of typical setpoints are given in Table 3. In each of these cases the carrier gas was air, maintained at a temperature of about  $320^{\circ}\text{F}$  ( $160^{\circ}\text{C}$ ). The total gas flow of the discharge units 31 and 32 was held at about 500 standard liters per minute. The coating station 59 was spaced about 0.22 inches (0.59 centimeter) above the moving glass ribbon 22. The extended region of predominantly tin oxide was deposited at the coating station 60 using the teachings of U S -A- 4,853,257.

[0087] The equation  $(\sqrt{a^2 + b^2})$  usually used by those skilled in the art to quantify the observability of color of an object is discussed by Hunter in Food Technology, Vol. 32, pages 100-105, 1967 and in The Measurement of Appearance, Wiley and Sons, New York, 1975. A coated glass product having a Hunter value of 12 or less is considered to exhibit no appreciable observable color. Listed in Table 3 under the column entitled Color Saturation Index is the measured Hunter value for the samples. As can be seen, all the samples had a color saturation index below 12.

Table 3

Sample #	MBTC Unit 61 mole %	MBTC Unit 62 mole %	MBTC Unit 64 mole %	TEOS Unit 61 mole %	TEOS Unit 62 mole %	TEOS Cell 64 mole %
1	0.280	0.190	0.490	0.050	0.050	0.020
2	0.290	0.300	0.600	0.100	0.160	0.300
3	0.350	0.200	0.940	0.300	0.300	0.270
4	0.400	0.200	0.940	0.300	0.300	0.330
5	0.600	0.758	0.790	0.390	0.400	0.350

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Table 3 (continued)

Sample #	MBTC Unit 61 mole %	MBTC Unit 62 mole %	MBTC Unit 64 mole %	TEOS Unit 61 mole %	TEOS Unit 62 mole %	TEOS Cell 64 mole %
6	0.500	0.600	1.200	0.265	0.300	0.100
MBTC means monobutyltintrichloride						
TEOS means tetraethoxysilane						

Sample #	TEP Unit 61 Unit mole %	TEP 62 mole %	TEP Unit 64 mole %	WATER Unit 61 mole %	WATER Unit 62 mole %	WATER Unit 64 mole %
1	0.300	0.100	0.025	0.170	0.600	0.600
2	0.280	0.110	0.039	0.180	0.330	0.630
3	0.280	0.120	0.070	0.150	0.610	0.370
4	0.280	0.100	0.050	0.150	0.610	0.370
5	0.266	0.120	0.066	0.150	0.180	0.640
6	0.400	0.300	0.288	0.400	1.000	1.000
TEP means triethylphosphite						

Sample #	GLASS TEMPERATURE °F	GLASS SPEED inches/min.	COLOR SATURATION INDEX	Gradient Thickness Å	Tin Oxide Thickness Å
1	1230	340	5.0	1200	4000
2	1234	340	5.0	1100	4000
3	1194	340	2.3	1250	3700
4	1200	340	3.6	1150	3650
5	1190	490	8.9	850	1750
6	1200	700	4.6	1000	1700.

## Claims

1. A transparent substrate (12) having a coating (14) thereon composed of at least two different metal oxides and having greater than 0 and up to 15 atomic percent of an element dispersed therethrough selected from the group consisting of phosphorus, aluminum and boron wherein the mixed metal oxide itself excludes phosphorus, aluminum and boron and the coating (14) has regions of continuously varying ratio of the different metal oxides as the distance from the substrate-coating interface (16) to the opposite surface (18) increases and with the substantial absence of strata of a fixed ratio of the different metal oxides.
2. The transparent substrate (12) of claim 1, wherein the coating (14) has 1 to 12 atomic percent of phosphorus dispersed therethrough.
3. The transparent substrate (12) of claims 1 or 2, wherein said metal oxides are selected from silicon, tin, titanium, tungsten, antimony and mixtures thereof.
4. The transparent substrate (12) of any of claims 1 to 3, wherein the substrate (12) is selected from glass or plastic.
5. The transparent substrate (12) of any of claims 1 to 4, wherein said substrate (12) is glass and the mixed metal oxides of the coating (14) are silicon oxide and tin oxide with a weight percent of 70-100 % of silicon oxide at the glass-coating interface (16) and a weight percent of 70-100 % tin oxide at the opposite coating surface and the element therethrough is phosphorus.
6. A method of depositing a vapor coating composition containing metal precursor compounds onto the surface of a moving substrate (23) by the steps of:

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directing the vapor coating composition toward a first predetermined position on the surface of the substrate (22),

5 moving a first portion of the vapor along a first region of the substrate surface in a first direction which is parallel with the direction in which the substrate (12) is moving, and a second portion of the vapor along a second region of the substrate surface in a second direction opposite to the first direction and maintaining the first portion of the coating composition on the first region of the substrate surface for a longer period of time than the second portion of the vapor on the second region of the substrate to coat the substrate (22), and exhausting the first and second portions of said vapor on each side of said first predetermined position after different periods of contact with the substrate surface, wherein the vapor coating composition contains at least two different metal containing precursors in an oxygen containing carrier gas to provide a coating having a continuously varying chemical composition of metal oxides as the distance from the substrate coating interface (16) to the opposite surface (18) increases.

7. The method of claim 6, wherein said substrate (22) is a glass substrate.

15 8. The method of claims 6 or 7, wherein the metal of the first metal containing precursor compound is silicon and the metal of one of the further metal containing precursor compounds is selected from tin, titanium, tungsten and antimony.

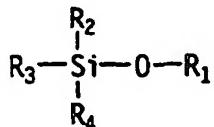
20 9. The method of any of claims 6 to 8, wherein the vapor coating composition contains accelerant(s) to increase the deposition rate of the mixed oxide coating.

10. The method of claim 9, wherein compounds containing phosphorus, boron, and/or aluminum are used as accelerants.

25 11. The method of claim 9, wherein the accelerant is a Lewis Acid or a Lewis Base.

12. The method of claim 9, wherein the accelerant is selected from triethylphosphite, trimethylphosphite, trimethylborate,  $\text{PF}_5$ ,  $\text{PCl}_3$ ,  $\text{BBr}_3$ ,  $\text{PCl}_5$ ,  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $(\text{CH}_3)_2\text{BBr}$ ,  $\text{SF}_4$ , and  $\text{HO}_3\text{SF}$ .

30 13. The method of any of claims 8 to 12, wherein said silicon containing precursor is defined by the following structural formula:



35 40 wherein  $\text{R}_1$  is a group which does not have an oxygen available to form a peroxide bond,  $\text{R}_2$  is the functional group giving the silicon containing precursor the ability to be easily converted to a silicon oxide coating,  $\text{R}_3$  is the bridging group to make multiple silicon atom molecules, and  $\text{R}_4$  is selected from hydrogen, halogen, -CN, -OCN, -PH<sub>2</sub>, alkyl or substituted alkyl radicals having from 1 to 10 carbon atoms, halogenated or perhalogenated alkyl radicals having from 1 to 10 carbon atoms, alkenyl or substituted alkenyl radicals having from 2 to 10 carbon atoms, alkynyl or substituted alkynyl radicals having from 2 to 10 carbon atoms, aryl or substituted aryl or aralkyl radicals having from 6 to 11 carbon atoms, alkoxide or substituted alkoxide radicals having from 1 to 10 carbon atoms, alkylphosphines and dialkyphosphines wherein the alkyl radical has from 1 to 10 carbon atoms,

45 50 14. The method of claim 13, wherein in the formula  $\text{R}_1$  is selected from the group consisting of:

alkyl, or substituted alkyl radicals having from 1 to 10 carbon atoms,  
alkenyl or substituted alkenyl radicals having from 2 to 10 carbon atoms,  
alkynyl or substituted alkynyl radicals having from 2 to 10 carbon atoms, and  
aryl or aralkyl or substituted aryl or aralkyl radicals having from 6 to 11 carbon atoms.

55 15. The method of claim 13, wherein in the formula  $\text{R}_2$  consists of:

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hydrogen, halogens, alkenyl or substituted alkenyl radicals having from 2 to 10 carbon atoms,  $\alpha$ -halogenated alkyl or perhalogenated alkyl radicals and substituted derivatives having 1 to 10 carbon atoms, and alkynyl or substituted alkynyl having from 2 to 10 carbon atoms.

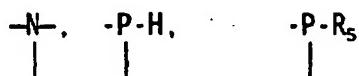
- 5 16. The method of claim 13, wherein in the formula  $R_3$  consists of:



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wherein  $R_5$  is an alkyl or substituted alkyl radical having from 1 to 10 carbon atoms,

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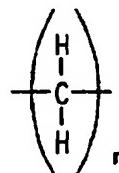


wherein  $R_5$  is defined as above,

20



25



30

where  $n$  is 1 to 10

35

17. The method of claim 13, wherein in the formula  $R_4$  is selected from:

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alkyl, or substituted alkyl radicals having from 1 to 10 carbon atoms,  
alkenyl or substituted alkenyl radicals having from 2 to 10 carbon atoms,  
alkynyl or substituted alkynyl radicals having from 2 to 10 carbon atoms, and  
aryl or aralkyl or substituted aryl or aralkyl radicals having from 6 to 11 carbon atoms.

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hydrogen, halogen, alkenyl or substituted alkenyl radicals having from 2 to 10 carbon atoms,  $\alpha$ -halogenated alkyl or perhalogenated alkyl radicals and substituted derivatives having 1 to 10 carbon atoms, and alkynyl or substituted alkynyl having from 2 to 10 carbon atoms.

50

19. The method of claim 13, wherein in the formula  $R_4$  is selected from:

alkoxide or substituted alkoxide radicals having from 1 to 10 carbon atoms, alkyl or substituted alkyl radicals having from 1 to 10 carbon atoms, -CN, -OCN, and phosphine, alkylphosphines, and dialkylphosphines, where in the alkyl radical has from 1 to 10 carbon atoms.

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20. The method of claim 13, wherein the silicon containing precursor compounds are selected from tetramethylcyclotetrasiloxane, tetramethyldisiloxane and triethoxysilane.

21. The method of any of claims 6 to 20, wherein said direction step is practiced at a second predetermined position

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spaced from and on one side of the first predetermined position and a third predetermined position spaced from the first and second predetermined positions such that the second predetermined position is between the first and third predetermined positions.

- 5        22. The method of any of claims 6 to 21, wherein the substrate (22) is coated in a chamber having a non-oxidizing atmosphere and a curtain of inert gas is provided to prevent the non-oxidizing atmosphere from moving to the predetermined positions wherein the curtain of inert gas and the predetermined positions therebetween define a coating position.
- 10      23. The method of claim 22, wherein the inert gas is nitrogen and the flows of nitrogen and the coating vapor are 350 to 700 standard liters per minute and the exhaust flow is 375 to 770 standard liters per minute.
- 15      24. The method of claim 22, wherein said chamber contains a bath of oxidizable molten metal and the substrate (22) is a glass ribbon supported on the molten metal and advanced through the chamber through the coating position.
- 20      25. The method of claim 24, wherein the speed of the glass ribbon is from 5.08 to 17.78 m/min (200-700 inches per minute) and the temperature of the glass ribbon is from 635°C to 675°C (1170°-1250° F).
- 25      26. The method of claim 6, wherein the first portion of the vapor is exhausted from one side of the first predetermined position in a distance x from said first predetermined position and the second portion of the vapor is exhausted from the other side of said first predetermined position in a distance y from said first predetermined position and the ratio x/y is in the range of 1.2 to 50.
- 30      27. The method of any of claims 6 to 26, wherein the substrate is of glass and the vapor coating composition contains a silicon containing precursor and a tin containing precursor and near the glass-coating interface (16) the coating (14) is predominantly silicon oxide, while at the opposite surface (18) farthest from the interface (16) of the coating (14) is predominantly tin oxide.
- 35      28. A coating apparatus (20, 59) for depositing a vapor coating composition containing metal precursor compounds onto the surface of a moving substrate (22) comprising:
- (i) means (25, 56, 58) for directing a vapor coating composition toward the surface of said substrate (22),  
   (ii) a first exhaust means (26) spaced in a distance "X" from said vapor directing means (25, 56, 58) on one side thereof;  
   35      (iii) a second exhaust means (28) spaced in a distance "y" from said vapor directing means (25, 56, 58) on the other side thereof and in alignment with said vapor directing means (25, 56, 58) and said first exhaust means (26),  
   (iv) a first discharge means (31) on the outboard side of the first exhaust means (26) for directing an inert gas toward the surface of said substrate (22),  
   40      (v) a second discharge means (32) on the outboard side of the second exhaust means (28) for directing an inert gas toward the surface of said substrate (22), each of the discharge means (31, 32) providing an inert gas curtain to prevent the coating vapors from moving from the coating zone between the discharge means (31, 32) into the atmosphere outside of the coating apparatus (20, 59), and also to prevent the atmosphere from moving into the coating zone.
- 45      29. The coating apparatus of claim 28, further comprising:  
   (vi) means for controlling flow volume capacity of said vapor coating composition directing means (25, 56, 58) and said first and second exhaust means (26, 28) such that the flow volume capacity of said vapor coating composition directing means (25, 56, 58) is different from that of at least one of said exhaust means (26, 28).
- 50      30. The coating apparatus of claims 28 or 29, wherein the ratio of x/y is in the range of 1.2 to 50.

55      **Patentansprüche**

1. Transparenter Träger (12) mit einer darauf angeordneten Beschichtung (14), die aus mindestens zwei unterschiedlichen Metalloxiden zusammengesetzt ist und mehr als 0 und bis zu 15 Atom-% eines darin dispergierten Elemen-

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tes enthält, ausgewählt aus der Gruppe bestehend aus Phosphor, Aluminium und Bor, wobei das gemischte Metalloxid selbst kein Phosphor, Aluminium und Bor enthält und die Beschichtung (14) Bereiche mit kontinuierlich variierendem Verhältnis der unterschiedlichen Metalloxide mit steigendem Abstand von der Grenzfläche (16) zwischen Träger und Beschichtung bis zur gegenüberliegenden Oberfläche (18) aufweist und wobei im wesentlichen keine Schichten mit festem Verhältnis der unterschiedlichen Metalloxide vorhanden sind.

- 5        2. Transparenter Träger (12) nach Anspruch 1, **dadurch gekennzeichnet, dass** die Beschichtung (14) 1 bis 12 Atom-% darin dispergierten Phosphor aufweist.

- 10      3. Transparenter Träger (12) nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Metalloxide aus Silicium, Zinn, Titan, Wolfram, Antimon und Mischungen derselben ausgewählt sind.

- 15      4. Transparenter Träger (12) nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** der Träger (12) aus Glas oder Kunststoff ausgewählt ist.

- 20      5. Transparenter Träger (12) nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** der Träger (12) aus Glas ist und die gemischten Metalloxide der Beschichtung (14) Siliciumoxid und Zinnoxid sind mit 70-100 Gew% Siliciumoxid an der Grenzfläche (16) Glas/Beschichtung und 70-100 Gew% Zinnoxid auf der gegenüberliegenden Beschichtungsoberfläche und dass das in der Beschichtung dispergierte Element Phosphor ist.

- 25      6. Verfahren zum Abscheiden einer dampfförmigen Beschichtungszusammensetzung, enthaltend Metallvorläuferverbindungen, auf der Oberfläche eines sich bewegenden Trägers (23) durch die Schritte:

Richten der dampfförmigen Beschichtungszusammensetzung auf eine erste vorbestimmte Stelle auf der Oberfläche des Trägers (22),

Bewegen eines ersten Teils des Dampfes über einen ersten Bereich der Trägeroberfläche in einer ersten Richtung, die parallel zur Richtung verläuft, in der sich der Träger (12) bewegt,  
Bewegen eines zweiten Teils des Dampfes über einen zweiten Bereich der Trägeroberfläche in einer gegenüber der ersten Richtung entgegengesetzten Richtung und

Aufrechterhalten des ersten Teils der Beschichtungszusammensetzung im ersten Bereich der Trägeroberfläche für eine längere Zeit als den zweiten Teil des Dampfes in dem zweiten Bereich des Trägers, um den Träger (22) zu beschichten, und

Absaugen der ersten und zweiten Teile des Dampfes an jeder Seite der ersten vorbestimmten Stelle nach unterschiedlichen Berührungszeiten mit der Trägeroberfläche, wobei die dampfförmige Beschichtungszusammensetzung mindestens zwei unterschiedliche Metallvorläuferverbindungen in einem sauerstoffhaltigen Trägergas enthält, um eine Beschichtung mit kontinuierlich variierender chemischer Zusammensetzung der Metalloxide mit steigendem Abstand von der Grenzfläche (16) Träger/Beschichtung zur gegenüberliegenden Oberfläche (18) zu schaffen.

- 40      7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** der Träger (22) ein Glasträger ist.

8. Verfahren nach Anspruch 6 oder 7, **dadurch gekennzeichnet, dass** das Metall der ersten metallhaltigen Vorläuferverbindung Silicium ist und das Metall einer der weiteren metallhaltigen Vorläuferverbindungen aus Zinn, Titan, Wolfram und Antimon ausgewählt ist.

- 45      9. Verfahren nach einem der Ansprüche 6 bis 8, **dadurch gekennzeichnet, dass** die dampfförmige Beschichtungszusammensetzung Beschleuniger enthält, um die Abscheidungsgeschwindigkeit der gemischten Oxidbeschichtung zu erhöhen.

- 50      10. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, dass** Verbindungen, die Phosphor, Bor und/oder Aluminium enthalten, als Beschleuniger verwendet werden.

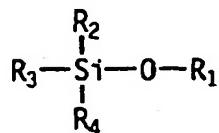
11. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, dass** der Beschleuniger eine Lewis-Säure oder eine Lewis-Base ist.

- 55      12. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, dass** der Beschleuniger aus Triethylphosphit, Trimethylphosphit, Trimethylborat,  $\text{PF}_5$ ,  $\text{PCl}_3$ ,  $\text{BBr}_3$ ,  $\text{PCl}_5$ ,  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $(\text{CH}_3)_2\text{BBr}$ ,  $\text{SF}_4$  und  $\text{HO}_3\text{SF}$  ausgewählt ist.

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13. Verfahren nach einem der Ansprüche 8 bis 12, dadurch gekennzeichnet, dass der siliciumhaltige Vorläufer der Strukturformel genügt:

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wobei in der Formel  $R_1$  eine Gruppe ist, die keinen zum Ausbilden einer Peroxidbindung verfügbaren Sauerstoff aufweist,  $R_2$  ist die funktionelle Gruppe, die dem siliciumhaltigen Vorläufer das Vermögen verleiht, leicht in eine Siliciumoxidbeschichtung umgewandelt zu werden,  $R_3$  ist die Brückengruppe zum Ausbilden von mehrere Siliciumatome enthaltenden Molekülen und  $R_4$  ist ausgewählt aus

15 Wasserstoff, Halogenen, -CN, -OCN, -PH<sub>2</sub>, Alkyl- oder substituierten Alkylgruppen mit 1 bis 10 Kohlenstoffatomen, halogenierten oder perhalogenierten Alkylgruppen mit 1 bis 10 Kohlenstoffatomen, Alkenyl- oder substituierten Alkenylgruppen mit 2 bis 10 Kohlenstoffatomen, Alkynyl- oder substituierten Alkynylgruppen mit 2 bis 10 Kohlenstoffatomen, Aryl- oder substituierten Aryl- oder Aralkylgruppen mit 6 bis 11 Kohlenstoffatomen, Alkoxid- oder substituierten Alkoxidgruppen mit 1 bis 10 Kohlenstoffatomen, Alkylphosphinen und Dialkylphosphinen, in denen 20 die Alkylgruppe 1 bis 10 Kohlenstoffatome aufweist.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass in der Formel  $R_1$  aus der aus:

25 Alkyl- oder substituierten Alkylgruppen mit 1 bis 10 Kohlenstoffatomen,  
Alkenyl- oder substituierten Alkenylgruppen mit 2 bis 10 Kohlenstoffatomen.  
Alkynyl- oder substituierten Alkynylgruppen mit 2 bis 10 Kohlenstoffatomen und  
Aryl- oder Aralkyl- oder substituierten Aryl- oder Aralkylgruppen mit 6 bis 11 Kohlenstoffatomen

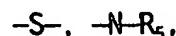
30 bestehenden Gruppe ausgewählt ist.

15. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass in der Formel  $R_2$  besteht aus:

35 Wasserstoff, Halogenen, Alkenyl- oder substituierten Alkenylgruppen mit 2 bis 10 Kohlenstoffatomen,  $\alpha$ -halogenierten Alkyloder perhalogenierten Alkylgruppen und substituierten Derivaten mit 1 bis 10 Kohlenstoffatomen und Alkynyl- oder substituierten Alkynylgruppen mit 2 bis 10 Kohlenstoffatomen.

16. Verfahren nach Anspruch 13, in der Formel  $R_3$  besteht aus:

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worin  $R_5$  eine Alkyl- oder substituierten Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ist,

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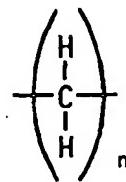
wobei  $R_5$  die zuvor angegebene Bedeutung hat,

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10 worin n = 1-10 ist

17. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass in der Formel R<sub>4</sub> aus:

Alkyl- oder substituierten Alkylgruppen mit 1 bis 10 Kohlenstoffatomen,  
 15 Alkenyl- oder substituierten Alkenylgruppen mit 2 bis 10 Kohlenstoffatomen,  
 Alkynyl- oder substituierten Alkynylgruppen mit 2 bis 10 Kohlenstoffatomen und  
 Aryl- oder Aralkyl- oder substituierten Aryl- oder Aralkylgruppen mit 6 bis 11 Kohlenstoffatomen

ausgewählt ist.

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18. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass in der Formel R<sub>4</sub> aus:

Wasserstoff, Halogen, Alkenyl- oder substituierten Alkenylgruppen mit 2 bis 10 Kohlenstoffatomen,  $\alpha$ -halogenierten Alkyl- oder perhalogenierten Alkylgruppen und substituierten Derivaten mit 1 bis 10 Kohlenstoffatomen  
 25 und Alkynyl- oder substituierten Alkynylgruppen mit 2 bis 10 Kohlenstoffatomen ausgewählt ist.

19. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass in der Formel R<sub>4</sub> ausgewählt ist aus:

30 Alkoxid- oder substituierten Alkoxidgruppen mit 1 bis 10 Kohlenstoffatomen, Alkyl- oder substituierten Alkylgruppen mit 1 bis 10 Kohlenstoffatomen, -CN, -OCN und Phosphin, Alkylphosphinen und Dialkylphosphinen, in denen die Alkylgruppe 1 bis 10 Kohlenstoffatome aufweist.

20. Verfahren nach Anspruch 13, dadurch gekennzeichnet, dass die siliciumhaltigen Vorläuferverbindungen aus Tetramethylcyclotetrasiloxan, Tetramethyldisiloxan und Triethoxysilan ausgewählt sind.

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21. Verfahren nach einem der Ansprüche 6 bis 20, dadurch gekennzeichnet, dass der Schritt des Richtens auf eine zweite vorbestimmte Stellung in Abstand von und an einer Seite der ersten vorbestimmte Stellung ausgeführt wird und das Richten auf eine dritte vorbestimmte Stellung in Abstand von der ersten und zweiten vorbestimmten Stellung so ausgeführt wird, dass sich die zweite vorbestimmte Stellung zwischen der ersten und dritten vorbestimmten Stellung befindet.

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22. Verfahren nach einem der Ansprüche 6 bis 21, dadurch gekennzeichnet, dass der Träger (22) in einer Kammer mit einer nichtoxidierenden Atmosphäre beschichtet wird und ein Vorhang aus Inertgas geschaffen wird, um zu verhindern, dass sich die nichtoxidierende Atmosphäre zu den vorbestimmten Stellungen bewegt, wobei der Vorhang aus Inertgas und die dazwischen liegenden vorbestimmten Stellungen eine Beschichtungsstelle definieren.

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23. Verfahren nach Anspruch 22, dadurch gekennzeichnet, dass das Inertgas Stickstoff ist und die Ströme von Stickstoff und der Beschichtungsdampf mit einer Geschwindigkeit von 350 bis 700 Standardliter/min strömen und der Abgasstrom 375 bis 770 Standardliter/min beträgt.

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24. Verfahren nach Anspruch 22, dadurch gekennzeichnet, dass die Kammer ein Bad aus oxidierbarem geschmolzenen Metall enthält und der Träger (22) ein von dem geschmolzenen Metall getragenes Glasband ist, das durch die Kammer in die Beschichtungsstellung vorwärts bewegt wird.

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25. Verfahren nach Anspruch 24, dadurch gekennzeichnet, dass die Geschwindigkeit des Glasbandes 5,08 bis 17,78 m/min (200-700 Inch/min) beträgt und die Temperatur des Glasbandes 635°C bis 675°C (1170°-1250° F) beträgt.

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26. Verfahren nach Anspruch 6, dadurch gekennzeichnet, dass der erste Teil des Dampfes von einer Seite der ersten vorbestimmten Stellung in einem Abstand x von der ersten vorbestimmten Stellung abgesaugt wird und dass der zweite Teil des Dampfes von der anderen Seite der ersten vorbestimmten Stellung in einem Abstand y von der ersten vorbestimmten Stellung abgesaugt wird und das Verhältnis von x/y im Bereich von 1,2 bis 50 liegt.

5 27. Verfahren nach einem der Ansprüche 6 bis 26, dadurch gekennzeichnet, dass der Träger aus Glas ist und die dampfförmige Beschichtungszusammensetzung einen siliciumhaltigen Vorläufer und einen zinnhaltigen Vorläufer enthält und nahe der Grenzfläche (16) Glas/Beschichtung die Beschichtung (14) hauptsächlich Siliciumoxid ist, während an der gegenüberliegenden Oberfläche (18) am weitesten entfernt von der Grenzfläche (16) Glas/Beschichtung die Beschichtung (14) hauptsächlich Zinnoxid ist.

10 28. Beschichtungsvorrichtung (20, 59) zum Abscheiden einer dampfförmigen Beschichtungszusammensetzung, enthaltend Metallvorläuferverbindungen, auf der Oberfläche eines sich bewegenden Trägers (22), enthaltend:

- 15 (i) Einrichtungen (25, 56, 58) zum Richten einer dampfförmigen Beschichtungszusammensetzung auf die Oberfläche des Trägers (22),  
(ii) eine erste Absaugeeinrichtung (26) in Abstand "x" von den Einrichtungen zum Richten des Dampfes (25, 56, 58) auf einer Seite derselben,  
(iii) eine zweite Absaugeeinrichtung (28) in Abstand "y" von den Einrichtungen zum Richten des Dampfes (25, 56, 58) auf der anderen Seite derselben und ausgerichtet mit den dampfrichtenden Vorrichtungen (25, 56, 58) und der ersten Absaugeeinrichtung (26),  
(iv) eine erste Auslasseinrichtung (31) auf der Außenseite der ersten Absaugeeinrichtung (26) zum Richten eines Inertgases auf die Oberfläche des Trägers (22),  
(v) eine zweite Auslasseinrichtung (32) auf der Außenseite der zweiten Absaugeeinrichtung (28) zum Richten eines Inertgases auf die Oberfläche des Trägers (22), wobei jede der Auslasseinrichtungen (31, 32) einen Inertgasvorhang schafft, um zu verhindern, dass sich die Beschichtungsdämpfe aus der Beschichtungszone zwischen Auslasseinrichtungen (31, 32) in die Atmosphäre außerhalb der Beschichtungsvorrichtung (20, 59) bewegen, und außerdem um zu verhindern, dass sich die Atmosphäre in die Beschichtungszone bewegt.

30 29. Beschichtungsvorrichtung nach Anspruch 28, weiterhin enthaltend:

- 35 (vi) Einrichtungen zum Steuern der Kapazität des Volumenflusses der Einrichtungen zum Richten (25, 56, 58) der dampfförmigen Beschichtungszusammensetzung und der ersten und zweiten Absaugeeinrichtungen (26, 28), so dass die Kapazität des Volumenflusses der Einrichtungen zum Richten (25, 56, 58) der dampfförmigen Beschichtungszusammensetzung sich von mindestens einer der Absaugeeinrichtungen (26, 28) unterscheidet.

40 30. Beschichtungsvorrichtung nach Ansprüchen 28 oder 29, dadurch gekennzeichnet, dass das Verhältnis von x/y im Bereich von 1,2 bis 50 liegt.

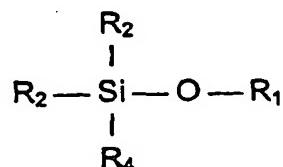
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#### Revendications

1. Substrat transparent (12) comportant un revêtement (14) composé d'au moins deux oxydes métalliques différents et comportant plus de 0 et jusqu'à 15 pour-cent atomiques d'un élément dispersé dans celui-ci choisi dans le groupe comprenant le phosphore, l'aluminium et le bore dans lequel l'oxyde métallique mixte en tant que tel exclut le phosphore, l'aluminium et le bore et le revêtement (14) comporte des zones de rapport des différents oxydes métalliques variant de façon continue au fur et à mesure que la distance de l'interface substrat-revêtement (16) à la surface opposée (18) augmente et en l'absence substantielle de couches d'un rapport fixe des différents oxydes métalliques.
2. Substrat transparent (12) suivant la revendication 1, dans lequel le revêtement (14) comporte 1 à 12 pour-cent atomiques de phosphore dispersé.
3. Substrat transparent (12) suivant l'une ou l'autre des revendications 1 et 2, dans lequel les oxydes métalliques précités sont choisis parmi le silicium, l'étain, le titane, le tungstène, l'antimoine et leurs mélanges.
4. Substrat transparent (12) suivant l'une quelconque des revendications 1 à 3, dans lequel le substrat (12) est choisi parmi le verre et le plastique.

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5. Substrat transparent (12) suivant l'une quelconque des revendications 1 à 4, dans lequel ledit substrat (12) est du verre et les oxydes métalliques mixtes du revêtement (14) sont de l'oxyde de silicium et de l'oxyde d'étain avec un pour-cent en poids de 70-100% d'oxyde de silicium à l'interface verre-revêtement (16) et un pour-cent en poids de 70-100% d'oxyde d'étain à la surface de revêtement opposée et l'élément dispersé est du phosphore.
10. Procédé de dépôt d'une composition de revêtement en phase vapeur contenant des composés précurseurs métalliques sur la surface d'un substrat mobile (23) par les étapes d'aménée de la composition de revêtement en phase vapeur vers une première position prédéterminée sur la surface du substrat (22), de déplacement d'une première partie de la vapeur le long d'une première zone de la surface du substrat dans une première direction qui est parallèle à la direction dans laquelle le substrat (12) est amené à se déplacer, et d'une seconde partie de la vapeur le long d'une seconde zone de la surface du substrat dans une seconde direction opposée à la première direction et en maintenant la première partie de la composition de revêtement sur la première zone de la surface du substrat pendant une période de temps plus longue que la seconde partie de la vapeur sur la seconde zone du substrat pour revêtir le substrat (22), et d'évacuation de la première et de la seconde partie de ladite vapeur de chaque côté de la première position prédéterminée précitée après différentes périodes de contact avec la surface du substrat, dans lequel la composition de revêtement en phase vapeur contient au moins deux différents précurseurs contenant du métal dans un gaz porteur contenant de l'oxygène pour former un revêtement ayant une composition chimique d'oxydes métalliques variant de façon continue au fur et à mesure que la distance de l'interface de revêtement de substrat (16) à la surface opposée (18) augmente.
15. Procédé suivant la revendication 2, dans lequel le substrat (22) précité est un substrat de verre.
20. Procédé suivant l'une ou l'autre des revendications 6 et 7, dans lequel le métal du premier composé précurseur contenant du métal est du silicium et le métal de l'un des autres composés précurseurs contenant du métal est choisi parmi l'étain, le titane, le tungstène et l'antimoine.
25. Procédé suivant l'une quelconque des revendications 6 à 8, dans lequel la composition de revêtement en phase vapeur contient un ou des accélérateurs pour éléver la vitesse de dépôt du revêtement d'oxyde mixte.
30. Procédé suivant la revendication 9, dans lequel on utilise des composés contenant du phosphore, du bore et/ou de l'aluminium comme accélérateurs.
35. Procédé suivant la revendication 9, dans lequel l'accélérateur est un acide de Lewis ou une base de Lewis.
40. Procédé suivant la revendication 9, dans lequel l'accélérateur est choisi parmi le triéthylphosphite, le triméthylphosphite, le triméthylborate,  $\text{PF}_5$ ,  $\text{PCl}_3$ ,  $\text{BBR}_3$ ,  $\text{PCl}_5$ ,  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $(\text{CH}_3)_2\text{BBr}$ ,  $\text{SF}_4$  et  $\text{HO}_3\text{SF}$ .
45. Procédé suivant l'une quelconque des revendications 8 à 12, dans lequel le précurseur contenant du silicium précité est défini par la formule structurale suivante :



dans laquelle  $\text{R}_1$  est un groupe qui ne comporte pas un oxygène disponible pour former une liaison peroxy,  $\text{R}_2$  est le groupe fonctionnel conférant au précurseur contenant du silicium la faculté d'être aisément converti en un revêtement d'oxyde de silicium,  $\text{R}_3$  est le groupe de pontage permettant de créer des molécules d'atomes de silicium multiples, et  $\text{R}_4$  est choisi parmi l'hydrogène, les halogènes, -CN, -OCN, -PH<sub>2</sub>, les radicaux alkyle ou alkyle substitués comportant de 1 à 10 atomes de carbone, les radicaux alkyle halogénés ou perhalogénés comportant de 1 à 10 atomes de carbone, les radicaux alcényle ou alcényle substitués comportant de 2 à 10 atomes de carbone, les radicaux aryle substitués ou aralkyle comportant de 6 à 11 atomes de carbone, les radicaux alcoolate ou alcoolate substitués comportant de 1 à 10 atomes de carbone, les alkylphosphines et les dialkylphosphines dans lesquelles le radical alkyle comporte de 1 à 10 atomes de carbone.

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14. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>1</sub> est choisi dans le groupe comprenant les radicaux alkyle ou alkyle substitués comportant de 1 à 10 atomes de carbone, les radicaux alcényle ou alcényle substitués comportant de 2 à 10 atomes de carbone, les radicaux alcynyle ou alcynyle substitués comportant de 2 à 10 atomes de carbone, et les radicaux aryle et aralkyle ou aryle et aralkyle substitués comportant de 6 à 11 atomes de carbone.

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15. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>2</sub> est choisi parmi l'hydrogène, les halogènes, les radicaux alcényle ou alcényle substitués comportant de 2 à 10 atomes de carbone, les radicaux alkyle  $\alpha$ -halogénés ou alkyle perhalogénés et les dérivés substitués comportant de 1 à 10 atomes de carbone, et les radicaux alcynyle ou alcynyle substitués comportant de 2 à 10 atomes de carbone.

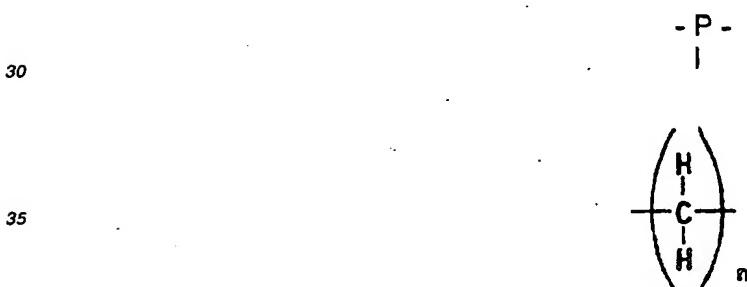
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16. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>3</sub> est un groupe



dans lequel R<sub>5</sub> est un radical alkyle ou alkyle substitué comportant de 1 à 10 atomes de carbone,



25  
dans lequel R<sub>5</sub> est tel que défini ci-dessus,



40  
où n vaut de 1 à 10.

17. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>4</sub> est choisi parmi les radicaux alkyle ou alkyle substitués comportant de 1 à 10 atomes de carbone, les radicaux alcényle ou alcényle substitués comportant de 2 à 10 atomes de carbone, les radicaux alcynyle ou alcynyle substitués comportant de 2 à 10 atomes de carbone, et les radicaux aryle et aralkyle ou aryle et aralkyle substitués comportant de 6 à 11 atomes de carbone.

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18. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>4</sub> est choisi parmi l'hydrogène, les halogènes, les radicaux alcényle ou alcényle substitués comportant de 2 à 10 atomes de carbone, les radicaux alkyle  $\alpha$ -halogénés ou alkyle perhalogénés et les dérivés substitués comportant 1 à 10 atomes de carbone, et les radicaux alcynyle ou alcynyle substitués comportant de 2 à 10 atomes de carbone.

50  
19. Procédé suivant la revendication 13, dans lequel dans la formule R<sub>4</sub> est choisi parmi les radicaux alcoolate ou alcoolate substitués comportant de 1 à 10 atomes de carbone, les radicaux alkyle ou alkyle substitués comportant de 1 à 10 atomes de carbone, -CN, -OCN, et les phosphine, alkylphosphines et dialkylphosphines, dans lesquelles le radical alkyle comporte de 1 à 10 atomes de carbone.

55  
20. Procédé suivant la revendication 13, dans lequel les composés précurseurs contenant du silicium sont choisis parmi le tétraméthylcyclotérasiloxane, le tétraméthyldisiloxane et le triéthoxysilane.

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21. Procédé suivant l'une quelconque des revendications 6 à 20, dans lequel l'étape d'amenée précitée est effectuée à une seconde position prédéterminée espacée et d'un côté de la première position prédéterminée et à une troisième position prédéterminée espacée de la première et de la seconde positions prédéterminées de telle sorte que la seconde position prédéterminée soit entre les première et troisième positions prédéterminées.
- 5 22. Procédé suivant l'une quelconque des revendications 6 à 21, dans lequel le substrat (22) est revêtu dans une chambre ayant une atmosphère non oxydante et un rideau de gaz inerte est prévu pour empêcher l'atmosphère non oxydante de se déplacer vers les positions prédéterminées dans lesquelles le rideau de gaz inerte et les positions prédéterminées disposées entre définissent une position de revêtement.
- 10 23. Procédé suivant la revendication 22, dans lequel le gaz inerte est de l'azote et les flux d'azote et de la vapeur de revêtement sont de 350 à 700 litres standards par minute et le flux d'évacuation est 375 à 770 litres standards par minute.
- 15 24. Procédé suivant la revendication 22, dans lequel la chambre précitée contient un bain de métal fondu oxydable et le substrat (22) est un ruban de verre supporté sur le métal fondu et amené à travers la chambre jusqu'à la position de revêtement.
- 20 25. Procédé suivant la revendication 24, dans lequel la vitesse du ruban de verre est de 5,08 à 17,78 m/min (200-700 pouces par minute) et la température du ruban de verre est de 635°C à 675°C (1170°-1250°F).
- 25 26. Procédé suivant la revendication 6, dans lequel la première partie de la vapeur est évacuée d'un côté de la première position prédéterminée à une distance x de cette première position prédéterminée et la seconde partie de la vapeur est évacuée de l'autre côté de ladite première position prédéterminée à une distance y de cette première position prédéterminée et le rapport x/y se situe dans la plage de 1,2 à 50.
- 30 27. Procédé suivant l'une quelconque des revendications 6 à 25, dans lequel le substrat est de verre et la composition de revêtement en phase vapeur contient un précurseur contenant du silicium et un précurseur contenant de l'étain et à proximité de l'interface verre-revêtement (16) le revêtement (14) est en prédominance de l'oxyde de silicium, alors qu'à la surface opposée (18) la plus éloignée de l'interface (16) du revêtement (14) de l'oxyde d'étain est en prédominance.
- 35 28. Appareil de revêtement (20, 59) pour déposer une composition de revêtement en phase vapeur contenant des composés précurseurs métalliques sur la surface d'un substrat mobile (22) comprenant :
- (i) des moyens (25, 56, 58) pour diriger une composition de revêtement en phase vapeur vers la surface dudit substrat (22),  
(ii) un premier moyen d'évacuation (26) espacé d'une distance "x" desdits moyens dirigeant la vapeur (25, 56, 58) d'un côté de ceux-ci,  
40 (iii) un second moyen d'évacuation (28) espacé d'une distance "y" desdits moyens dirigeant la vapeur (25, 56, 58) de l'autre côté de ceux-ci et dans l'alignement des moyens dirigeant la vapeur (25, 56, 58) et du premier moyen d'évacuation (26) précités,  
(iv) un premier moyen de décharge (31) du côté extérieur du premier moyen d'évacuation (26) pour diriger un gaz inerte vers la surface du substrat (22) précité,  
45 (v) un second moyen de décharge (32) du côté extérieur du second moyen d'évacuation (28) pour diriger un gaz inerte vers la surface dudit substrat (22), chacun des moyens de décharge (31, 32) formant un rideau de gaz inerte pour empêcher les vapeurs de revêtement de se déplacer de la zone de revêtement entre les moyens de décharge (31, 32) dans l'atmosphère à l'extérieur de l'appareil de revêtement (20, 59), et également pour empêcher l'atmosphère de se déplacer dans la zone de revêtement.
- 50 29. Appareil de revêtement suivant la revendication 28, comprenant de plus :  
(vi) un moyen pour commander une capacité de volume d'écoulement des moyens dirigeant la composition de revêtement en phase vapeur (25, 56, 58) et des premier et second moyens d'évacuation (26, 28) précités de telle sorte que la capacité de volume d'écoulement desdits moyens dirigeant la composition de revêtement en phase vapeur (25, 56, 58) soit différente de celle d'au moins un desdits moyens d'évacuation (26, 28).
- 55 30. Appareil de revêtement suivant l'une ou l'autre des revendications 28 et 29, dans lequel le rapport de x/y se situe

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dans la plage de 1,2 à 50.

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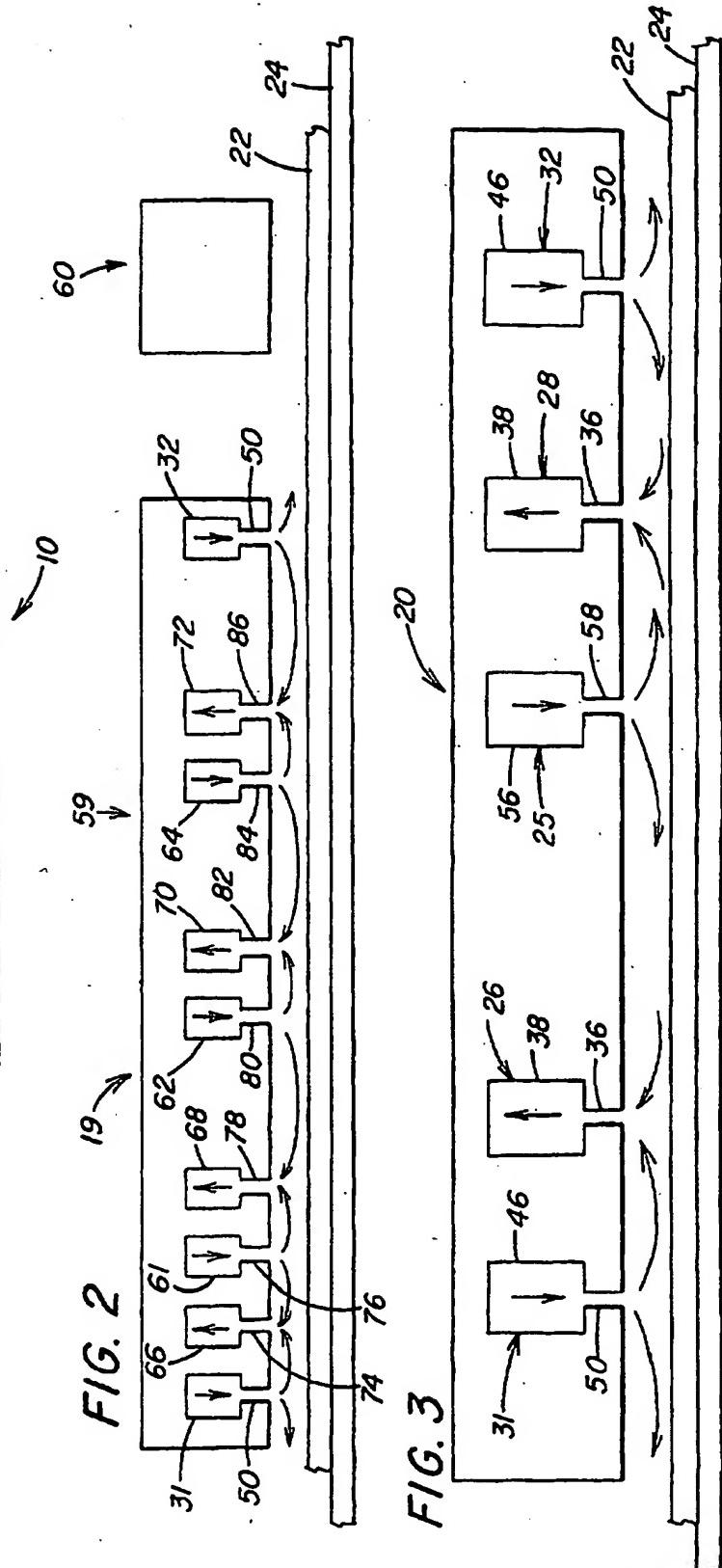
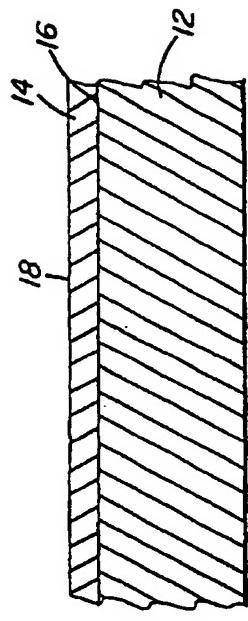
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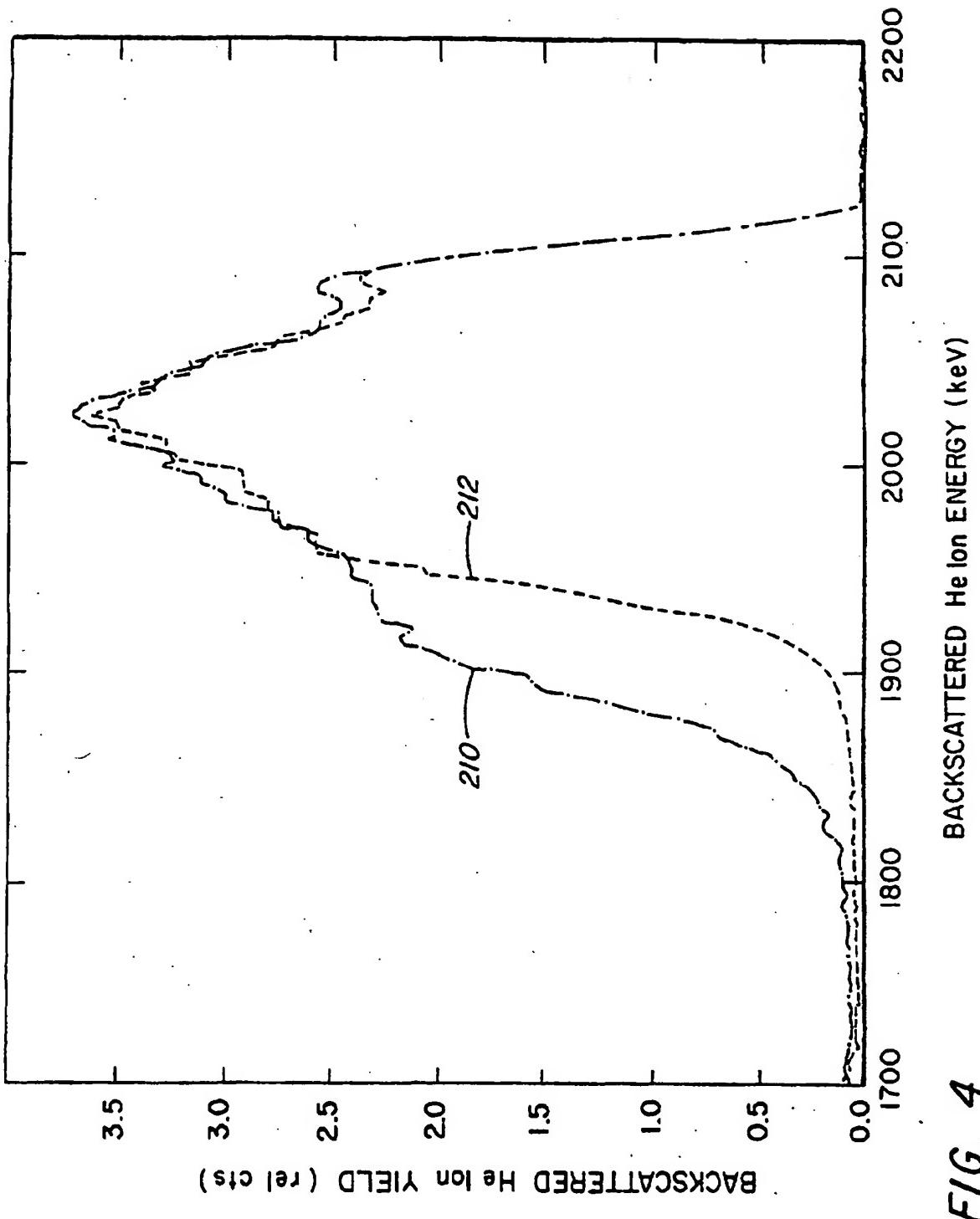


FIG. 4

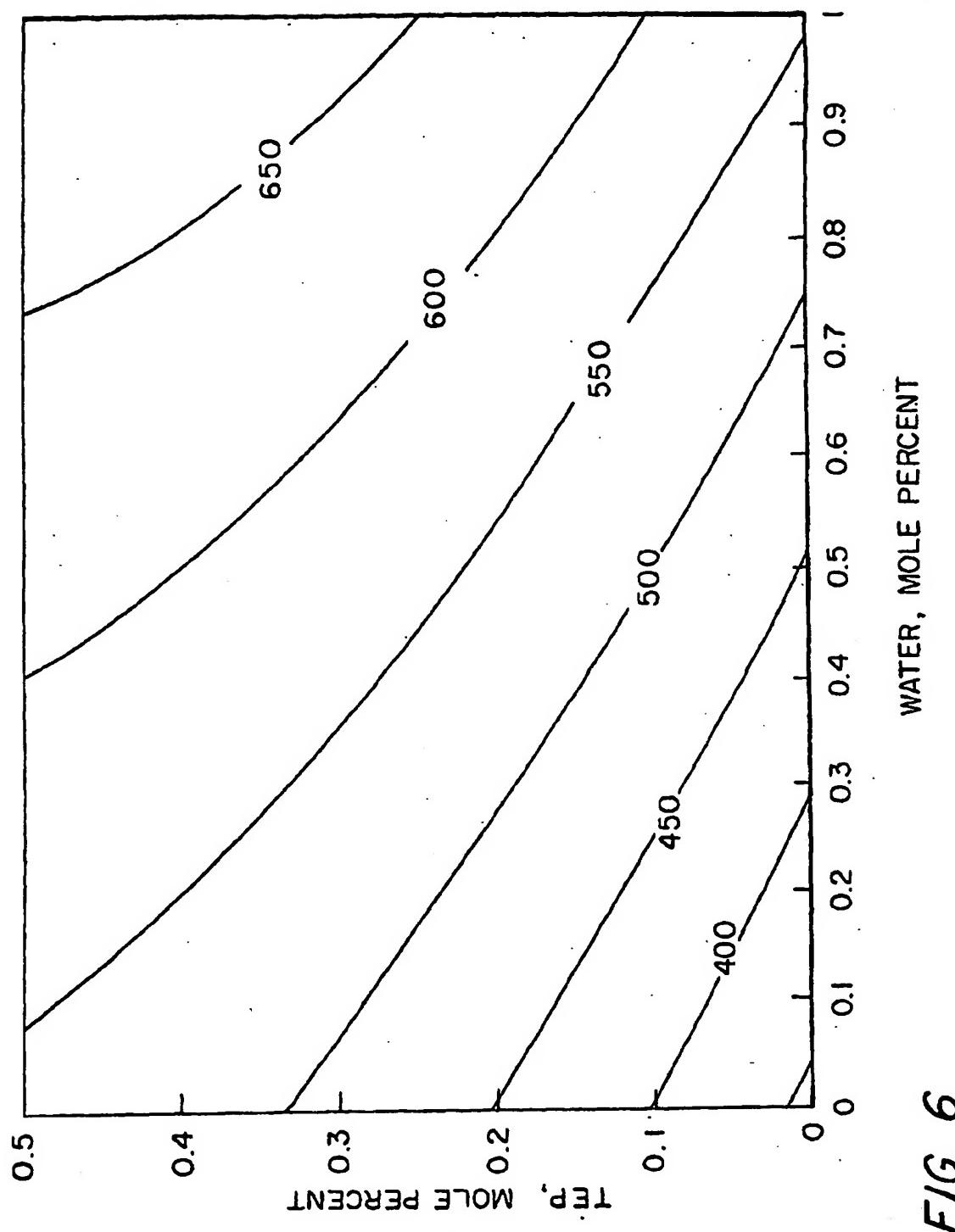


FIG. 6